Amendments to the Drawings:

Sheets 1-4, including Figs. 1-6, replace the originally filed sheets 1-4. The replacement sheets replace the original hand drawn figures with formally drafted figures for the sake of clarity. Additionally, in replacement Figure 1, previously omitted reference number **9** has been added; in replacement Figure 4, previously omitted reference number **33** has been added; and in replacement Figure 5, reference number **30** has been changed to the correct reference number **20**.

Attachment: Replacement Sheets

REMARKS

This Preliminary Amendment amends the present application as follows:

1) a Cross-Reference to Related Application section has been added;

2) the spelling has been changed to American English from British English, and the grammar revised to standard American English grammar;

3) the citation for United States Patent 4,763,985, which was missing the last number in the parent application, has been corrected;

4) the format of the listings of the United States Patents has been changed to include the family names of the first inventors;

5) the application has been reformatted for United States patent practice;

6) the appropriate citations for the trademarks disclosed have been revised to indicate whether they are registered in the United States;

7) new figures have been prepared to replace the hand drawn figures in the parent application for the sake of clarity and to add some reference numbers for elements from the original disclosure; and

8) the claim set has been revised.

No new matter has been added by these revisions. Entry of this Preliminary Amendment is hereby requested.

CONCLUSION

Claims 14-39 are now pending in the above-identified United States patent application. All claims are believed to be in condition for examination and allowance, and an indication of such is earnestly solicited. If there are any issues that can be addressed by telephone with the Applicant's representative, the Examiner is encouraged to contact the undersigned.

The Commissioner is hereby authorized to charge payment of any fees associated with this communication to Deposit Account No. 19-2090.

Respectfully submitted,

SHELDON & MAK
A Professional Corporation

Date: January 13, 2006

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VERSION WITH MARKINGS TO SHOW CHANGES MADE

IN THE DISCLOSURE:

CROSS-REFERENCE TO RELATED APPLICATIONS

This application is a national phase filing of International Patent Application No. PCT/EP2003/012948 entitled "Process for Manufacturing Retroreflective Printed Material," filed November 19, 2003, which claims priority from European Patent Application No. 02425785.9 filed December 19, 2002; the contents of which are incorporated by reference herein in their entirety.

~~**DESCRIPTION**~~

FIELD

The present invention ~~refers~~ is related to a process for manufacturing retroreflective printed material.

BACKGROUND

~~It is known that~~ The use of safety garments comprising retroflective printing ~~products used for safety garments can reduce~~ reduces the risk of accidents, especially for ~~some particular categories of people, such as, for example: firemen, paramedicals, adult and children playing sports~~ persons in certain professions such as for example firefighters and paramedics, as well as for athletes.

~~The only commercial~~ Commercial products suitable for use with reflective garments ~~have~~ generally ~~been~~ consist of ~~the single-colored type~~ a single color. For example, ~~in US-A-4.763.98, US-A-5.283.101 and US-A-5.738,746~~ United States Patent 4,763,985 to Bingham, 5,283,101 to Li and 5,738,746 to Billingsley et al., disclose launderable retroflective grey-

colored products ~~are disclosed~~. ~~The following patents describe the possibility of obtaining colored effects and printed effects as well as reflective quality.~~

A number of patents disclose processes for producing colored effects and printed effects, as well as reflectivity.

~~A retroreflective structure described in US-A- 5.962.121 is capable of exhibiting a decorative effect both during the day and during the night, and particularly a rainbow-colored effect.~~ For example, United States Patent 5,962,121 to Mori discloses a retroreflective structure capable of exhibiting a decorative rainbow-colored effect during both daytime and nighttime.

~~In US-A-4.605.461 a method is described~~ United States Patent 4,605,461 to Ogi discloses a process for transferring a retroreflective pattern onto a fabric. United States Patent 4,102,562 to Harper et al. discloses ~~Retroreflective~~ retroreflective images formed on garments and other substrates. ~~are described in US-A-4.102.562, while US-A- 5.508.105~~ United States Patent 5,508,105 to Orensteen et al. discloses a thermal printing system and a colorant/binder for printing frangible, retroreflective sheeting material. ~~US-A-5.620.613~~ United States Patent 5,620,613 to Olsen discloses the printing of designs or emblems on garments, ~~comprising~~ where the design comprises a monolayer of microspheres, and a first printing of ~~the~~ a first color layer with a silk-screening system. When the prints of the first color are ~~all~~ dried, ~~the~~ subsequent colors can be printed through the same technique until the design on the layer of microspheres is completed. A similar patent for decorating textile surfaces, ~~US-A-5.679.198~~ United States Patent 5,679,198 to Olsen et al., discloses a multi-step printing of

many colors prepared with a polyester resin and an isocyanate hardener, dried before printing the following color ~~and so on~~. Also in ~~US-A- 5.785.790~~ United States Patent 5,785,790 to Olsen et al., the same silk-screening multi-color printing technique is used with a system of colors made of polyester resin hardened with isiocyanate.—

——Many other United States patents ~~(US-A-3.689.346, US-A-5.643.400, US-A-4.082.426, US-A-2.231.139, US-A-2.422.256, US-A- 4.656.072, US-A-4.952.023) describe~~ disclose processes for producing retroreflective materials, including United States Patents 2,231,139 to Reininger, 2,422,256 to Phillippi, 3,689,346 to Rowland, 4,082,426 to Brown, 4,656,072 to Coburn, Jr. et al., 4,952,023 to Bradshaw et al. and 5,643,400 to Bernard et al.. ~~US-A-6.120.636~~ United States Patent 6,120,636 to Nilsen et al. discloses a high speed, low cost process for producing sheets patterned with drawings and emblems using a rotary screen printing system with cylinders and hardening with ~~U.V.~~ UV lamps.

~~Despite the above-described prior art situation, there still remain restrictive limits for printing retroreflecting products using many colors, with a high production speed, production flexibility and without ecological problems. From what is known, no one has previously found a practical way to produce a printed retroreflective product for fashion use using designs containing one or many colors. Some have proposed silk- screen printing with one water-based color or solvent- based colors but the above inventions are~~ There does not appear, however, to be a practical process for producing a printed retroreflective product for fashion garments using designs containing one or more than one color. While, processes using silk-screen printing with one

water-based color or solvent-based colors have been proposed, these processes are unfeasible for reproducing fashion designs with many colors upon a retroreflective material.

Additionally, many patents disclose the use of screen-printing technology, such as for example United States Patent 5,620,630 to Onishi et al. and United States Patent 5,785,790 to Olsen et al., among others. With this screen-printing technology, however, it is impossible to print designs on garments comprising many colors while maintaining design and color accuracy on a layer of microspheres to produce retroreflecting materials. The same is true of a rotary screen-printing system disclosed in United States Patent 6,120,636 to Nilsen et al. Therefore, there remains a need for a process for printing retroreflecting products comprising one or more than one color, with a high production speed, production flexibility and without producing significant amounts of pollution.

~~In the present invention as pointed out in Claim 1, a temporary support sheet is provided, with a monolayer of transparent glass microspheres partially embedded in a layer of softened polymer to a depth ranging between one- quarter and one-half of the microsphere diameter, as conventionally used in retroreflective materials, as described in US-A-3.700.305 and US-A-6.416.188. Then, after coating the layer of microspheres with a thin thermo-adhesive polymer film, a design is thermo-transferred onto the microsphere surface.~~

~~Two kinds of commercial transfer-printed design may be used: (a) designs with sublimate pigments printed on a paper base; or~~

~~(b) designs having a polymer film supported by a release paper base or a polymer film base, such as for example a film of polypropylene.~~

~~In case of transferring a printing with sublimate pigments (a), the transfer temperature ranges between 180°C and 220°C. A temperature close to 220°C causes a maximum yield of color transferring, but also a partial transferring of colors at lower temperatures may give a satisfactory aesthetic design on the final retroreflective product.~~

~~In case of transferring a printed polymer film as shown in (b), the layer of microspheres is beforehand coated with a thin layer of bicomponent polyurethane. The thin layer of polyurethane resin dried but not cured operates as thermo-adhesive between microspheres and printed film. In this case, the print transfer temperature is lower than 150°C, and preferably between 100°C and 120°C.~~

~~As regards the above-described prior art, many patents use the screen-printing technology (US-A-5.620.630, US-A-5.785.790 and others). With this printing system, it is concretely impossible to print designs containing many colors while maintaining the design accuracy and the perfect fitting of various printed colors, not as is normally done on a textile support but on a layer of microspheres to produce retroreflecting materials. The same considerations can be done with a rotary screen-printing system (US-A-6.120.636).~~

~~The present invention instead provides a flexible, ecological, easy-to-apply process, for obtaining printed retroreflective products especially, but not restrictively, for fashion garments where rich designs and colors are demanded and appreciated. The printing transfer machine needs a low-cost~~

~~investment compared with other printing processes; no auxiliary equipment and small floor space are required, and no pollution or obnoxious effluence is produced. Moreover, the availability of commercial transfer printed papers is considerable.~~

~~A special feature of the present invention is the possibility of vacuum application of a thin aluminium reflecting layer after the printing process. In this case, it is possible to avoid the application of a transparent dielectric mirror though maintaining a sufficient reflective intensity for a printed fashion product.~~

~~Over the printing or over the reflective aluminium layer, a polyurethane two-components resin is coated, dried and laminated over a fabric. The polyurethane resin coating may be substituted with a thin layer of a hot-melt adhesive being applied.~~

~~The present invention will be better described by some preferred embodiments thereof, provided as a non- limiting example, with reference to the enclosed drawings, in which:~~

SUMMARY

According to one embodiment of the present invention, there is provided a process for manufacturing retroreflective printed material, the process comprising a) providing a composite comprising a temporary support sheet with a layer of microspheres partially embedded in the temporary support sheet such that the surfaces of the microspheres are partially exposed; b) applying a reflecting layer on the microspheres; c) applying a priming layer either on the partially exposed surfaces of the microspheres or on the reflecting layer; d) transferring a printed design layer from a transfer medium with the printed design on the primer layer and separating the transfer medium without the printed design from the printed design layer; e) applying a binder layer

on the printed design layer; f) applying a base fabric on the binder layer and separating the temporary support sheet from the layer of microspheres, thereby creating the retroreflective printed material, where the reflecting layer is either applied on the microsphere surface of the composite between the priming layer and the microsphere surface of the composite, or is applied on the printed design layer between the printed design layer and the binder layer. In one embodiment, the microspheres are transparent glass microspheres. In another embodiment, the microspheres have a diameter, and the microspheres are partially embedded in the temporary support sheet to a depth ranging between 40% and 50% of the microsphere diameter.

In another embodiment, the temporary support sheet comprises a coating film and a backing sheet. In a preferred embodiment, the coating film is selected from the group consisting of a polymeric coating film, polyethylene, polypropylene, a low-density polyethylene thermo-adhesive film and an acrylic auto-adhesive film. In a preferred embodiment, the backing sheet is selected from the group consisting of kraft paper and polyester film. In a preferred embodiment, providing a composite comprises placing the microspheres on the temporary support sheet by a process selected from the group consisting of printing, cascading, transferring and screening.

In another embodiment, the reflecting layer is a dielectric mirror layer applied on the microsphere surface of the composite, and where the priming layer is applied on the dielectric mirror layer. In another embodiment, the reflecting layer is a light reflecting material layer applied on the printed design layer, and where the binder layer is applied on the light reflecting material layer. In a preferred embodiment, the light reflecting

material layer is a vapor coating of a metal or thin reflective aluminium film layer applied by vacuum deposition.

In one embodiment, the priming layer is selected from the group consisting of a thin layer of transparent thermo-adhesive bicomponent polyurethane resin and a resin of a water polyether polyurethane dispersion. In another embodiment, the printed design layer from a transfer medium with the printed design comprises a plurality of colors. In another embodiment, the transfer medium with the printed design comprises a design with sublimate pigments. In a preferred embodiment, transferring a printed design comprises thermo-transferring at a temperature between 180°C and 220°C.

In another embodiment, the transfer medium with the printed design comprises a design printed on a polymer film. In a preferred embodiment, transferring a printed design comprises thermo-transferring at a temperature between 100°C and 120°C.

In one embodiment, the binder layer is selected from the group consisting of a bicomponent polyurethane resin and a thin layer of a hot-melt adhesive.

According to another embodiment of the present invention, there is provided a retroreflective printed material made according to the process of the present invention. In one embodiment, there is provided an article of clothing, sportswear or footwear comprising the retroreflective printed material of the present invention.

According to another embodiment of the present invention, there is provided a retroreflective printed material comprising: a) a microspheres layer; b) a priming layer on the microsphere layer; c) a printed design layer on the primer layer; d) a binder layer on the printed design layer; e) a base fabric on the binder

layer; and f) a reflecting layer; where the reflecting layer is either between the microsphere layer and the priming layer, or is between the printed design layer and the binder layer. In one embodiment, the microspheres are transparent glass microspheres. In another embodiment, the reflecting layer is a dielectric mirror layer. In one embodiment, the reflecting layer is a vapor coating of a metal or thin reflective aluminium film layer. In another embodiment, the priming layer is selected from the group consisting of a thin layer of transparent thermo-adhesive bicomponent polyurethane resin and a resin of a water polyether polyurethane dispersion. In one embodiment, the printed design layer comprises a plurality of colors. In another embodiment, the binder layer is selected from the group consisting of a bicomponent polyurethane resin and a thin layer of a hot-melt adhesive.

FIGURES

These and other features, aspects and advantages of the present invention will become better understood with regard to the following description, appended claims, and accompanying figures which depict some of the steps in certain embodiments of the process of the present invention, where:

~~- Figure 1 shows a schematic sectional view of an article of clothing 10 at the final stage of production according to the present invention ;~~

~~- Figure 2 shows a schematic view of a continuous apparatus for doctor blade on roll coating of a supported layer of microspheres;~~

~~- Figure 3 shows a schematic view of a production machine for transferring printed designs using sublimation pigments;~~

~~- Figure 4 shows a schematic carrier web, which secures microspheres thereon in a desired temporary arrangement;~~

~~- Figure 5 is a plan view showing a schematic design of a printed paper; and~~

~~- Figure 6 schematically shows the drawing transfer of Fig. 5 from the original printed sheet to the surface of the layer of microspheres.~~

Figure 1 is a partial cross- sectional view of a portion of an article of clothing that is partially delaminated from the temporary support sheet, according to the present invention;

Figure 2 is a schematic drawing of a machine that can be used in the process of the present invention;

Figure 3 is a schematic drawing of a machine for transferring printed designs with sublimate pigments according to the present invention;

Figure 4 is a partial cross-sectional view of a composite of a temporary support sheet with partially embedded microspheres according to the present invention;

Figure 5 is a schematic plan view of a transfer medium with a printed design suitable for use with the present method; and

Figure 6 is a schematic drawing showing the design on a transfer medium with the printed design, as shown in Figure 5, being transferred to a surface comprising a layer of microspheres as the printed transferred image, while the transfer medium without the printed design is partially released from the printed transferred image, according to the present invention.

~~In the invention as described and shown, a specific terminology is used for better clarity. However, the invention is not constrained to the specific terms being chosen and it is~~

~~obvious that every chosen term comprises every technical equivalent that generates a similar behavior.~~

DESCRIPTION

According to one embodiment of the present invention, there is provided a process for manufacturing retroreflective printed material. The process can be performed at a rapid production rate, is flexible and does not produce significant amounts of pollution. The machinery used with the present process requires a relatively low investment of capital and a relatively small amount of floor space compared with other printing processes, and requires no auxiliary equipment. Moreover, commercial transfer media suitable for use with the present process are widely available. The present invention can be used to produce retroreflective printing on a substrate, such as for example fabric for garments. The present process is especially suited for printing complex designs in multiple colors on retroreflecting garments for the fashion industry, such as for example, clothing, sportswear, footwear and fashion accessories, as well as for producing retroreflective printing on products used in high risk professions where high visibility increases safety. The present process involves transferring a printed design comprising one or more than one color on a paper or plastic base onto the surface of a temporary support sheet having a layer of partially embedded microspheres and coated with a priming layer.

Though certain steps of the process are disclosed and shown in the Figures, the steps are not intended to be limiting nor are they intended to indicate that each step depicted is essential to the process, but instead are exemplary steps only. Further, though the present invention is disclosed in part with reference

to certain examples, which show some of the features and advantages of the invention, the ingredients and the specific amounts of the ingredients disclosed, as well as other conditions and details are not intended to be limiting to the scope of the present invention. Other ingredients, amounts and conditions can be used, as will be understood by those with skill in the art with reference to this disclosure. Certain embodiments of the process will now be disclosed in detail.

All dimensions specified in this disclosure are by way of example only and are not intended to be limiting. Further, the proportions shown in these Figures are not necessarily to scale. As will be understood by those with skill in the art with reference to this disclosure, the actual dimensions of any device or part of a device disclosed in this disclosure will be determined by its intended use.

Unless otherwise specified, all amounts expressed in the examples are in parts by weight.

According to one embodiment of the present invention, there is provided a process for manufacturing retroreflective printed material. In one embodiment, the present process comprises, first, providing a composite of a temporary support sheet comprising a layer of microspheres partially embedded in the temporary support sheet such that the surface of the microspheres are partially exposed. In a preferred embodiment, the microspheres are transparent glass microspheres. In another preferred embodiment, the temporary support sheet comprises a layer of softened polymer, and the microspheres partially embedded in the softened polymer to a depth ranging between 20% and 50% of the microsphere diameter, as conventionally used in retroreflective materials, and as disclosed in United States

Patent 3,700,305 to Bingham and United States Patent US 6,416,188 B1 to Shusta et al. among other sources. Next, a design from a commercial transfer medium is thermo-transferred onto the microsphere surface of the composite.

Two kinds of commercial transfer media with a printed design can be used with the present method: 1) designs with sublimate pigments printed on a paper base; and 2) designs printed on a polymer film supported by a release paper base or a polymer film base, such as for example polypropylene film. When thermo-transferring a design with sublimate pigments, the transfer temperature ranges between 180°C and 220°C. A transfer temperature close to 220°C causes a maximum yield of color transfer, but a partial transfer of colors at lower temperatures can also give a satisfactory aesthetic design on the final retroreflective printed product.

When thermo-transferring a design printed on polymer film, the present process comprises applying a priming layer on the microsphere surface of the composite. In one embodiment, the priming layer is as a thin layer of transparent thermo-adhesive bicomponent polyurethane resin having a thickness of about 1 micron. The priming layer is partially cured by drying, and operates as thermo-adhesive between microspheres and the design printed on the polymer film. In this embodiment, the transfer temperature is lower than 150°C. In a preferred embodiment, the transfer temperature is between 100°C and 120°C.

The present process further comprises applying a reflecting layer applied on the partially exposed surfaces of the microspheres. In one embodiment, the reflecting layer comprises a substantially transparent dielectric mirror layer. In another embodiment, the reflecting layer comprises a light reflecting

material layer applied on the printed design layer over the microsphere surface of the composite. In a preferred embodiment, the light reflecting material layer is a thin reflective aluminium film layer by vacuum deposition after the printing process. When the reflective aluminium film layer is applied, the dielectric mirror layer is not necessary as the product produced has a sufficient reflective intensity for a printed fashion product without a dielectric mirror layer.

In another embodiment, the process further comprises applying a binder layer on the printed design layer, or on the light reflecting material layer if present. The binder layer is partially dried and a base fabric is applied to the binder layer. In one embodiment, the binder layer is a bicomponent polyurethane resin. In another embodiment, the binder layer is a thin layer of a hot-melt adhesive.

~~Fig. 4 is a cross sectional view of a carrier web 20, which secures glass microspheres 1 on a temporary transport support. The carrier web used as a sheet material is produced as described in US-A-4.102.562. The microspheres 1 used in the present invention typically have an average diameter in the range of about 30 to 200 microns and a refractive index of about 1.7 to 2.0. Preferably the glass microspheres 1 are arranged substantially in a monolayer on a temporary carrier sheet 20, which comprises a backing sheet 3 and a polymeric coating film 2. The polymeric coating 2 is a softenable material such as polyethylene, polypropylene and the like. The stiff backing sheet 3 could be kraft paper, polyester film and the like.~~

~~The microspheres 1 may be arranged upon the temporary carrier sheet 20 by printing, cascading, transferring, and screening or any convenient transfer process.~~

~~The microspheres 1 can be embedded in the carrier sheet 20 with a pressure roll or by heating the softened polymer, to a depth between about 20% to 40% of their average diameter.~~

Referring now to Figure 4, there is shown a partial cross-sectional view of a composite of a temporary support sheet with partially embedded microspheres according to the present invention. As can be seen, the temporary support sheet 20 comprises a coating film 2 and a backing sheet 3. The coating film 2 is a softenable material, such as for example a polymer. In one embodiment, the coating film 2 is a polymeric coating film. In another embodiment, the coating film 2 is a polymer selected from the group consisting of polyethylene and polypropylene. In a preferred embodiment, the coating film is a low-density polyethylene thermo-adhesive film. In another embodiment, the polymeric coating film is an acrylic auto-adhesive film. The backing sheet 3 comprises a stiff material. In one embodiment, the backing sheet is selected from the group consisting of kraft paper and polyester film. The temporary support sheet 20 can be produced by known processes, such as disclosed in United States Patent 4,102,562 to Harper et al.

The microspheres 1 used in the present invention will typically have an average diameter in the range of about 30 to 200 microns and a refractive index of between about 1.7 to 2.0. Preferably, the microspheres 1 are arranged substantially in a monolayer on the temporary support sheet 20. The microspheres 1 can be placed on the temporary support sheet 20 by printing,

cascading, transferring, screening or any other suitable process, as will be understood by those with skill in the art with reference to this disclosure. After placement, the microspheres 1 are embedded in the temporary support sheet 20 to a depth of between about 20% to 50% of their average diameter, such as for example using a pressure roller or by heating the softened polymer, yielding a composite of the temporary support sheet and microspheres 33.

~~Fig. 1 shows a sectional view, not to scale, of a portion of an article of clothing 10 that is partially delaminated from the carrier web comprising the polymeric coating 2 and the kraft paper or polyester film backing 3.~~

~~Disposed adjacent to the non-embedded glass surface of the microspheres 1 is a transparent dielectric mirror 4, a priming layer 5 of bi-component polyurethane of about 1 micron.~~

~~The layer 6 reduces the printed layer, whose thickness is less than 0.1 microns, in the case of sublimate pigments (a) and less than 0.5 microns in the case of transfer printing supported by a polymer film (b).~~

~~With reference again to Fig. 1, the printed design over the microspheres 1 is covered with a layer 7 made of vacuum-nebulised aluminium, or other light reflecting material. Obviously, in this case the layer of transparent dielectric mirror 4 is not necessary.~~

~~With reference again to Fig. 1, finally, a binder layer 8 will provide an adequate thermal adhesion with a base fabric 9, for example a polyester/cotton fabric, a nylon knitted fabric made of a Lycra® or other textile bases.~~

Referring now to Figure 1, there is shown a partial cross-sectional view of a retroreflective printed material 10 being

produced according to the present invention, as it is partially separated from the temporary support sheet 20 part of the composite of a temporary support sheet and microspheres 33. As can be seen, in one embodiment, a dielectric mirror layer 4 is disposed adjacent to the surface of the microspheres 1. Further, a priming layer 5 covers the microsphere surface of the composite 33, or, as shown, the dielectric mirror layer 4 when present. A printed design layer 6 is disposed on the priming layer, and preferably has a thickness of less than 0.1 micron in the case of designs with sublimate pigments printed on a paper base, and less than 0.5 microns in the case of designs having a polymer film supported by a release paper base or a polymer film base. In one embodiment, the printed design layer 6 is covered with a light reflecting material layer 7, such as for example a vapor coating of a metal, a vacuum-nebulized reflective aluminium film layer, or other suitable light reflecting material, as will be understood by those with skill in the art with reference to this disclosure. When the light reflecting material layer 7 is present, the dielectric mirror layer 4 is not necessary. Finally, a binder layer 8 covers the printed design layer 6, or the light reflecting material layer 7 when present, and binds a base fabric 9, such as for example a polyester/cotton fabric, a nylon knitted fabric made of a Lycra® (E. I. du Pont De Nemours and Company, Wilmington, DE US) or other textile base fabrics.

~~Fig. 2 and 3 are schematic drawings of apparatus used in the invention, which include a well-known rotary machine 29 for thermal transfer printing of the calender type (manufactured by Lemaire, Roubaix, France or Monti Officine, Thiene, Italy).~~

~~The composite microspheres layer 33 (supplied by cylinder 40), as described in Fig. 4, together with the printed~~

~~paper 30 (supplied by cylinder 24) are pressed between heated cylinder 27 and felt 26 in a continuous process (Fig. 3). Out of the machine, the paper 31 without the design is wound on cylinder 25 on one side, and the printed layer of microspheres 34 is wound on cylinder 32 on the other side.~~

~~In Fig. 2 the continuous printing process is made on the composite material 33 (supplied by cylinder 40) coated (in machine 23) with a polyurethane layer 5 (supplied by cylinder 22) as shown in Fig. 3. At the end of the process, a product 34 is obtained that is wound on cylinder 28.~~

Referring now to Figure 2 and Figure 3, there are shown schematic drawings of machines that can be used in the process of the present invention. As can be seen, the machines comprise a rotary machine 29 for transfer printing using a heated calender, such as for example, a rotary machine manufactured by Lemaire & Cie, Roubaix, France or Monti Officine Fonderie S.p.A., Thiene, Italy.

Figure 3 is a schematic drawing of a machine for transferring printed designs with sublimate pigments according to the present invention. As can be seen, the composite layer 33 supplied by cylinder 40, and the transfer medium with the printed design 30 supplied by a cylinder 24 are pressed together between a heated cylinder 27 and a felt 26 in a continuous process. At the end of the process, the machine dispenses the transfer medium without the printed design 31 wound on a cylinder 25, and the printed transferred image 34 wound on another cylinder 32.

Figure 2, is a schematic drawing of a continuous machine for doctor-knife coating the microsphere surface of a composite of a temporary support sheet and microspheres 33. As can be seen, the continuous printing process coats the composite of a temporary

support sheet and microspheres 33 supplied by a cylinder 40 with a priming layer 5 supplied by a cylinder 22 in a coating machine 23. At the end of the process, the machine dispenses the printed transferred image 34 wound on a cylinder 28.

~~Fig. 5 is a schematic plan view showing a transfer paper 30 printed with nature image containing 8 colors a, b, c, d, e, and f. The commercial offer of transfer printed paper is remarkable. This type of paper is widely used in many applications in textile industries but also in several areas such as accessories, furniture, interior decorations, motor vehicles and the like.~~

~~Samples of the present invention have been prepared using transfer printed papers from Transfertex GmbH, Kleinostheim, Germany and a special polypropylene printed film Decotrans® from Miroglio Sublitex, Alba, Italy.~~

Referring now to Figure 5, there is shown a schematic plan view of a transfer medium with a printed design 30 suitable for use with the present method. In this example, the design comprises images derived from natural subjects, and comprises 8 colors labeled a, b, c, d, e, f, g and h. Transfer media with printed designs of this type are widely available commercially, and are widely used in many applications in the textile industries, as well as in other fields, such as for example, in the fields of household accessories, furniture, interior decorations, and motor vehicles. Samples of retroreflective printed material were prepared according to the present invention using transfer media from Transfertex GmbH & Co., Kleinostheim, Germany and a polypropylene printed film (Decotrans™) from Miroglio S.p.A.--Sublitex, Alba, Italy.

~~Fig. 6 is view of partially removed released paper 31 without the design from the carrier web, which secures microspheres covered with the printed transferred image 34.~~

Referring now to Figure 6, there is shown a schematic drawing showing the design on a transfer medium with the printed design 30, as shown in Figure 5, being transferred to a surface comprising a layer of microspheres as the printed transferred image 34, while the transfer medium without the printed design 31 is partially released from the printed transferred image 34, according to the present invention.

~~The invention will be further explained by the following illustrative examples, which serve the purpose of showing the features and advantages of this invention. However, the ingredients and the specific amounts recited therein, as well as other conditions and details are intended to be not limiting of the scope of the present invention. Unless otherwise specified, all amounts are expressed in the examples are in parts by weight.~~

~~**EXAMPLE 1**~~

EXAMPLE 1

A monolayer of glass microspheres having diameters between 40 and 100 microns was produced by ~~Cascading~~ cascading the microspheres ~~on a Kraft~~ onto a kraft paper covered with an acrylic auto-adhesive film. ~~produced the monolayer of glass microspheres having diameters between 40 and 100 microns.~~ The layer of microspheres was then transferred onto a temporary support comprising a backing sheet of polyester covered with a coating of low- density polyethylene thermo-adhesive film ~~of 50-micron thickness~~ 50 microns thick. The transfer was made with a heated calender as shown in ~~Fig. 3~~ Figure 3, at a cylinder

temperature of 140°C. The contact time was 5 seconds and the pressure between the heated cylinder and the felt was 5 bars, ~~in order to obtain a penetration of the microspheres onto the polyethylene film of about 40% of their diameter. The exposed surface of the microspheres was then coated with a transparent dielectric mirror as described in US-A-3.700.305~~ which yielded a penetration of the microspheres into the temporary support sheet of about 40% of their diameter, thereby creating a composite of a temporary support sheet and microspheres.

A dielectric mirror layer, as described in United States Patent 3,700,305 to Bingham, was then applied to the exposed surface of the microspheres on the composite. The amount of the dielectric mirror layer was about 4 g/m^2.

A ~~bi-component~~ bicomponent polyurethane priming layer was next applied over the electric mirror layer, by coating the dielectric mirror layer with ~~a~~ the solution ~~of the following~~ according to formulation 1 with a ~~doctor knife-coating~~ doctor - knife coating machine or a graved-roll coating machine [[:]].

~~Ingredients~~	~~Parts by Weight~~
~~Polyurethane resin ("B-10" from Coim)~~	~~100~~
~~Curing agent ("Imprafix TH" from Bayer)~~	~~5~~
~~Methylethylketone~~	~~150~~
~~**Formulation 1**~~	

Formulation 1

Ingredients	Parts by Weight
Polyurethane resin ("B 10" from COIM S.p.A. Milan, Italy)	100
Curing agent ("Imprafix TH" from Bayer Material Science AG, Leverkusen, Germany)	5
Methylethylketone	150

The ~~resin has been~~ priming layer was dried and partially cured at 110°C. ~~The amount of transparent film layer is about 4 g/m2.~~

At the end of the oven as ~~described in the Fig. 2~~ disclosed with respect to Figure 2, the product ~~is running~~ was fed into the calendar, heated ~~at~~ to 130°C, and laminated with ~~the~~ a transfer medium with the printed design comprising a polypropylene printed film ~~Decotrans®~~ (Decotrans™) having the design shown in ~~Fig. 5~~ Figure 5. The contact time ~~is~~ was about 10 ~~sec.~~ Seconds. Then the polypropylene portion of the transfer medium without the printed design and the printed ~~microspheres~~ transferred image were ~~separately unwound~~ separated. Next, a binder layer comprising a solution of polyurethane resin according to formulation 2, was applied to the printed transferred image at a thickness of approximately 125 microns when wet.

~~Subsequently, a solution of the following polyurethane formulation 2, using a knife on roll coating, was coated over the printed layer at approximately a 125-micron thick wet substance.~~

~~Ingredients~~	~~Parts by Weight~~
~~Polyurethane resin ("B 10" from Coim)~~	~~100~~
~~Curing agent ("Desmodur RFE" from Bayer)~~	~~5~~
~~Methylethylketone~~	~~40~~
~~Melamine curing agent ("C6" from Coim)~~	~~3~~
~~**Formulation 2**~~	

Formulation 2

Ingredients	Parts by Weight
Polyurethane resin ("B 10" from COIM S.p.A. Milan, Italy)	100
Curing agent ("Desmodur REQUEST FOR EXAMINATION" from Bayer Material Science AG, Leverkusen, Germany)	5
Methylethylketone	40
Melamine curing agent ("C6" from COIM S.p.A. Milan, Italy)	3

The polyurethane resin binder layer ~~has been~~ was partially dried at 80°C. At the end of the oven, the surface of the still tacky binder layer resin was ~~superposed~~ superimposed and calendered ~~on~~ onto a ~~white polyester/cotton~~ base fabric containing 65% ~~of~~ polyester and 35% ~~of~~ cotton. After calendering

the laminated ~~compound~~ fabric at 100°C and a pressure of 5 bars, the ~~compound~~ fabric was cooled and the ~~polyester film~~ temporary support sheet was peeled off, yielding a fabric with the retroreflective printed design. ~~Subsequently the printed retroreflective textile~~ This printed transferred image was cured at 150°C in an oven for ~~2 min~~ about 2 minutes to finish curing the polyurethane resin binder layer, and yielding the retroreflective printed material.

~~**EXAMPLE 2**~~

EXAMPLE 2

A monolayer of glass microspheres having similar characteristics as those mentioned in Example 1 was deposited ~~onto the low density 50-micron~~ on a temporary support sheet comprising a coating film of low-density polyethylene film of 50 micron thickness supported by a backing sheet of ~~40-micron polyester carrier~~ 40 micron polyester film. ~~The glass spheres-covered carrier was then heated for 2-4 min at 150°-160°C and penetrated into the softened polyethylene. The glass microspheres thus became embedded in polyethylene for about 40% of the sphere diameter and formed a monolayer therein with little or no space between spheres. The coating with a transparent dielectric mirror and the subsequent steps of production were the same as described in Example 1~~ The composite of the temporary support sheet and microspheres was then heated for between 2 and 4 minutes at between 150°C and 160°C, which yielded a penetration of the microspheres into the polyethylene film of about 40% of their diameter, with little or no space between microspheres. The exposed surface of the microspheres was then coated with a dielectric mirror layer, and the subsequent steps of the process were the equivalent to those disclosed in Example 1.

~~**EXAMPLE 3**~~

EXAMPLE 3

~~The~~ A monolayer of glass microspheres having diameters between 40 and 100 microns was produced by cascading the microspheres onto a thick release paper covered with an acrylic auto-adhesive film as described in Example 2 of ~~US-A-4.075.049~~ United States Patent 4,075,049 to Wood. ~~The resulting microspheres binder composite was doctor-knife coated with a water polyether polyurethane dispersion having the following formulation 3.~~ A priming layer comprising a resin of a water polyether polyurethane dispersion according to formulation 3 was doctor-knife coated on the composite of the temporary support sheet and microspheres.

~~Ingredients~~	~~Parts by Weight~~
~~Polyurethane water based resin ("Idrocap 930"from Icap)~~	~~100~~
~~Curing agent ("Icaplink X3" from Icap)~~	~~5~~
~~Water~~	~~40~~
~~Thickening agent ("Idrocap 200" from Icap)~~	~~a.r.~~
~~**Formulation 3**~~	

Formulation 3

Ingredients	Parts by Weight
Polyurethane water based resin ("Idrocap 930" from Icap-sira Chemicals and Polymers S.p.A., Milan, Italy)	100
Curing agent ("Icaplink X3" Icap-sira Chemicals and Polymers S.p.A., Milan, Italy)	5
water	40
thickening agent ("Idrocap 200" from Icap-sira Chemicals and Polymers S.p.A)	a.r.

The amount of wet priming layer resin was about 10 g/m^2 and was adjusted with the ~~doctor knife~~ doctor-knife profile, resin dilution and viscosity. The amount of ~~dry~~ dried film was about 3 g/m^2. The priming layer resin was partially cured at 110°C. At the end of the oven as ~~described in Fig. 2~~ disclosed with respect to Figure 2, the product was ~~run~~ fed into the calender, heated ~~at~~ to 130 °C, and laminated with ~~the printed~~ a transfer medium with the printed design comprising a polypropylene printed film ~~Decotrans®~~ (Decotrans™) having the design shown in ~~Fig. 5~~ Figure 5. The contact time was about 10 ~~sec~~ seconds. Then, the polypropylene ~~without the design and the printed microspheres were unwound~~ portion of the transfer medium without the printed design and the printed transferred image were separated. The resulting printed ~~composite was worked according to whether it comes covered or not covered with a vapour coating of a metal such as aluminium light reflecting material 7 in Fig. 1~~ transferred image was further processed according to whether it comprised a light reflecting material layer, in this case a vapor

coating of a metal such as an aluminium light reflecting material. When the printed transferred image comprised the light reflecting material layer, the subsequent steps of the process were the same as disclosed in Example 1. When the composite did not comprise a light reflecting material layer, the subsequent steps of the process comprised applying a polyurethane binder layer by knife coating, and then applying a textile to the binder layer.

~~In case the composite was metallised, the subsequent process was the same as described in Example 1. In case the composite was not metalleisd, the subsequent treatment was polyurethane knife coating and textile lamination.~~

The aesthetic printing effect without the light reflecting ~~aluminium~~ material layer ~~is~~ was very regular but the average initial reflectivity was between 8 and 15 cd/(luxm)~~, that was a low value for a technical product but that remained effective for a fashion fabric~~. The ~~metal~~ light reflecting material layer of the ~~printed retroreflective fabric that was metallised favourably affects the design colors and~~ product with the light reflecting material layer favorably affected the design colors and the reflectivity ~~is~~ was greater than 50 cd/(luxm), making the product suitable for use in connection with high risk professions.

~~**EXAMPLE 4**~~

EXAMPLE 4

~~The~~ A monolayer of glass microspheres having diameters between 40 and 100 microns was produced by cascading the microspheres onto a thick release paper covered with an acrylic auto-adhesive film as described in Example 2 of United States Patent 4,075,049 to Wood. ~~The exposed surface of the microspheres~~

~~was then coated with a transparent dielectric mirror.~~ A dielectric mirror layer was then applied to the exposed microsphere surface of the composite of a temporary support sheet and microspheres. ~~Then, the~~ Next, a transfer print process was made using a commercial transfer medium with a printed design with sublimate pigments ~~(a)~~ from Transfertex GmbH & Co.~~,~~ ~~Kleinostheim, Germany~~. The transfer temperature was about 185°C, however,~~. In fact~~ the heated roll was in contact with the back of the transfer ~~paper~~ medium, and therefore, the real temperature of the ~~glass~~ microsphere layer of the composite was higher than the real temperature of the ~~printed paper~~ transfer medium, but sufficient ~~for obtaining~~ to obtain a good yield of ~~pigments~~ pigment sublimation onto the exposed ~~upper~~ surface of the microspheres. ~~The composite material was metallised and coated using Formulation 2 with a knife on roll coating machine.~~ Next, a metallized light reflecting material layer was applied to the printed transferred image using formulation 2 with a doctor-knife coating machine. ~~The resin~~ Next, a polyurethane resin binder layer was applied and was partially dried at 80°C. At the end of the oven, the surface of the still tacky binder layer resin was ~~superposed~~ superimposed and calendered on a ~~white polyester/cotton~~ base fabric containing 65% ~~of~~ polyester and 35% ~~of~~ cotton. After calendering the laminated ~~compound~~ base fabric at 100°C and a pressure of 5 bars, the ~~compound~~ fabric was cooled and the ~~polyester film~~ temporary support sheet was peeled off. ~~Subsequently the printed retroreflective textile~~ Then, retroreflective printed fabric was cured at 150°C in an oven for about 2 ~~min~~ minutes to ~~for finally~~ finish curing the ~~resin~~ binder layer.

IN THE ABSTRACT:

~~The present application relates to a retroreflective printed product on fabrics a for use in clothing, sportswear, footwear and accessories with a lightreflecting effect, with good design flexibility which ensure trend-setting fashion sense as well as safety sense due to high visibility. More particularly, the invention deals with a continuous, flexible printing process without pollution and effluence, which use a printed mono- or multi-coloured design on paper base or other plastic base to be transferred over the surface of a layer (2) of glass microspheres (1) that are partially embedded in a support sheet (2) and coated with a very thin layer (5) of transparent thermo-adhesive bi-component polyurethane.~~

A process for manufacturing retroreflective printed material, the process comprising a) providing a composite comprising a temporary support sheet with a layer of microspheres partially embedded in the temporary support sheet such that the surfaces of the microspheres are partially exposed; b) applying a reflecting layer on the microspheres; c) applying a priming layer either on the partially exposed surfaces of the microspheres or on the reflecting layer; d) transferring a printed design layer from a transfer medium with the printed design on the primer layer and separating the transfer medium without the printed design from the printed design layer; e) applying a binder layer on the printed design layer; f) applying a base fabric on the binder layer and separating the temporary support sheet from the layer of microspheres, thereby creating the retroreflective printed material. A retroreflective printed material made according to the process.